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**ON THE SOLUBILITY OF
THE CAMPHORATES OF SOME OF THE HEAVY METALS**

by

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A Thesis Submitted for the Degree of

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Although many of the camphorates have been prepared and known for a long time, very little is to be found in the literature in regard to their solubilities in other liquids than water. Kemper prepared lithium, ammonium, sodium, calcium, barium and zinc camphorates. The zinc salt he found to be insoluble, and the others to be soluble, in water. The lithium salt was also soluble in alcohol. Manning and Edwards prepared aluminum, strontium, nickel, manganese, mercuric and ferric camphorates, of which only the camphorate of manganese was soluble in cold, but not in hot water. The present work was taken up with the view of finding other solvents than water for the camphorates of the heavy metals and to accurately determine the solubility of the copper salt in water. The camphorates of copper, zinc, manganese, lead and nickel were chosen for this experiment. The camphoric acid from which these salts were made was prepared according to Wreden (Ann. 163, 323), by boiling 150 grams of camphor with two liters of nitric acid (sp.gr. 1.27) for 72 hours on the water bath. The acid thus obtained was purified by neutralizing its aqueous solution with ammonia, reprecipitating with hydrochloric acid and finally by recrystallizing from hot water. The camphorates of copper, lead, nickel and manganese were made by Manning's method (Am.Ch.J. 10, 235), which was slightly modified in that

equivalent quantities of substances were used in all cases and that sodium hydroxide was substituted for potassium hydroxide. To a standard 10% solution of sodium hydroxide was added the theoretical amount of camphoric acid required for neutralization. The solution of sodium camphorate thus obtained was divided into four parts which were treated respectively with the required amounts of lead acetate, manganous sulphate, copper sulphate and zinc sulphate for double decomposition. The nickel camphorate was made according to Edwards (Am. Ch. J. 10, 235) by treating pure nickel hydroxide with an excess of camphoric acid in a small amount of water heated on the water bath.

On account of lack of time the solubility of copper camphorate in water only was accurately determined. Water was saturated at 15°C. with copper camphorate, two liters of the resulting solution evaporated to dryness in the presence of a little nitric acid, and the residue ignited and dissolved in a small amount of nitric acid. This nitric acid solution was diluted with water and the copper weighed as electrolytic copper. One part of copper camphorate was found to dissolve in 11,700 parts of water at 15°C. In the remainder of the experiment one cubic centimeter of the solvent was used and estimated amounts of the salt were added by comparing with weighed samples. In table No. 1, I means insoluble; i.e. the smallest amount of the salt that could be conveniently added did not dissolve.

If less than 1% dissolved it is denoted by ss. If a salt dissolves at all it is either sparingly soluble as denoted by ss or it is freely soluble to at least 10%, which is indicated by S. d indicates that the salt was decomposed with an accompanying change of color or effervescence and that the decomposition products did not dissolve. Table No. 2, which contains only the effective solvents of table No. 1, is added for convenience.

Table No.1.

<u>Solvents</u>	<u>Copper camphor- ate</u>	<u>Lead camphor- ate</u>	<u>Zinc camphor- ate</u>	<u>Mangan- ese cam- phorate</u>	<u>Nickel camphor- ate</u>
Hydrocarbons					
Amylene	I	I	I	I	I
Benzene	I	I	I	I	I
Gasoline	I	I	I	I	I
Kerosene	I	I	I	I	I
Ligroin	I	I	I	I	I
Limonene	I	I	I	I	I
Mesitylene	I	I	I	I	I
Naphthalene	I	I	I	I	I
Paraffine	I	I	I	I	I
Pentane	I	I	I	I	I
Turpentine	I	I	I	I	I
Vaseline	I	I	I	I	I
Esters					
Acetoacetic ester	I	I	I	I	I
Amyl acetate	I	I	I	I	I
Amyl benzoate	I	I	I	I	I
Amyl butyrate	I	I	I	I	I
Amyl valerianate	I	I	I	I	I
Benzoylacetic ester	I	I	I	I	I
Bornyl formate	I	I	I	I	I
Ethyl acetate	I	I	I	I	I
Ethyl benzoate	I	I	I	I	I
Lactic ester	I	I	I	I	-
Malonic ester	I	I	I	I	I
Methyl acetate	I	I	I	I	I
Methyl salicylate	I	I	I	I	I
Phenyl acetate	I	I	I	I	I
Methyl cyanacetate	I	I	I	I	I
Ethyl cyanacetate	I	I	I	I	I
Ethyl chlorcarbonate	I	I	I	I	I
Monochlor ethyl acetate	I	I	I	S	I
Substituted					
Hydrocarbons					
Amyl nitrate	I	I	I	I	I
Amyl sulphate	I	I	I	I	I
Benzo trichloride	I	I	d	d	I
Brom benzene	I	I	I	I	I
Bromoform	I	I	I	I	I
Carbon disulphide	I	I	I	I	I
Carbontetrachloride	I	I	I	I	I
Chloroform	I	I	I	I	I

<u>Solvents</u>	<u>Copper camphor- ate</u>	<u>Lead camphor- ate</u>	<u>Zinc camphor- ate</u>	<u>Mangan- ese cam- phorate</u>	<u>Nickel camphor- ate</u>
Substituted					
Hydrocarbons					
Ethylene dibromide	I	I	I	I	I
Isobutyl nitrate	I	I	I	I	I
Methyl sulphate	I	I	I	I	I
Methyl iodide	I	I	I	I	I
Nitroethane	I	I	I	I	I
Alcohols					
Allyl	I	I	I	I	I
Ethyl	I	I	I	I	I
Dichlor propyl	I	I	I	I	I
Glycerol	I	I	I	I	I
Isoamyl	I	I	I	I	I
Isobutyl	I	I	I	I	I
Methyl	I	I	I	I	I
Menthol	I	I	I	I	I
Propyl	I	I	I	I	I
Phenols					
Cresol	I	I	I	I	I
Guaiacol	I	I	I	I	I
Phenol	I	I	I	I	I
Resorcinol	I	I	I	I	I
Acids					
Acetic	S	S	S	S	S
Acrylic	S	S	S	S	S
Benzoic	S	S	S	S	S
Butyric	S	S	S	S	S
Camphoric	I	I	I	I	I
Propylic	S	S	SS	S	S
Stearic	S	S	S	S	S
Valeric	S	S	I	S	I
Valeric and water	S	S	S	S	S
Acid anhydrides					
Acetic	I	I	I	I	I
Benzoic	S	S	S	S	S
Camphoric	I	I	I	I	I
Phthalic	I	I	I	I	I

Solvents	Copper camphor- ate	Lead camphor- ate	Zinc camphor- ate	Mangan- ese cam- phorate	Nickel camphor- ate
Aldehydes					
Acetaldehyde	ss	I	I	I	I
Anisicaldehyde	I	I	I	I	I
Benzaldehyde	I	I	I	I	I
Benzoic aldehyde	I	I	I	I	I
Chloral	d	I	I	I	I
Formaldehyde	I	I	I	I	I
Oenanthol	I	I	I	I	I
Paraldehyde	ss	I	I	I	I
Valerianaldehyde	I	I	I	I	I
Ketones					
Acetone	I	I	I	I	I
Camphor	I	I	I	I	I
Methyl ethyl ketone	I	I	I	I	I
Acid Amides					
Acetamide	I	ss	I	ss	ss
Formamide	s	s	s	s	s
Amines					
Amylamine	s	I	s	s	s
Benzylamine	I	I	I	I	I
Dibenzylamine	I	-	-	-	-
Diphenyl amine	I	I	I	I	I
Dipropyl amine	I	I	I	I	I
Ethylene diamine	d	ss	s	ss	ss
Toluidine	I	-	-	-	-
Tripropylamine	I	I	I	I	I
Triphenylamine	I	I	I	I	I
Nitriles					
Benzoyl cyanide	I	-	-	-	-
Lactic acid nitrile	I	I	I	I	I
Ethylene cyanide	I	I	I	I	I
Mandelic nitrile	I	I	I	I	I
Methyl cyanide	I	I	I	I	I
Other Bases					
Picoline	I	I	I	I	I
Piperidine	I	I	I	I	I
Pyridine	I	I	I	I	I
Quinoline	I	I	I	I	I
Alkaloids					
Conine	I	I	I	I	I
Nicotine	I	I	I	I	I

Solvents	Copper camphor- ate	Lead camphor- ate	Zinc camphor- ate	Mangan- ese cam- phorate	Nickel camphor- ate
Fixed Oils					
Cottonseed oil	I	I	I	I	I
Linseed oil	I	I	I	I	I
Olive oil	I	I	I	I	I
Acetates					
Sodium acetate	I	I	I	ss	I
Potassium acetate	ss	ss	ss	ss	ss
Ammonium acetate	s	s	s	s	s
Acetic esters	I	I	I	I	I
Miscellaneous					
Acetyl chloride	d	I	I	I	I
Aldehyde cyanhydrin	I	I	I	I	I
Chloral hydrate	I	I	I	I	I
Benzoyl chloride	d	d	d	d	d
Ethyl ether	I	I	I	I	I
Ethyl sulphhydride	d	I	d	I	I
Monochlorhydrin	I	I	I	I	-
Sugar	I	I	I	I	I
Thiophene	I	I	I	I	I
Benzene - ammonia	I	-	-	-	-
Ethyl acetate - "	I	-	-	-	-
Aniline - ammonia	I	-	-	-	-
Aqueous oxalic acid	d	-	-	-	-
" succinic "	d	-	-	-	-
Phenyl mustard oil	I	I	I	I	I
Inorganic					
Antimony trichloride	I	I	I	I	I
Aqueous ammonia	s	s	s	s	s
Ammonium sulphate	s	s	s	s	s
Phos. trichloride	d	d	d	d	d
" sulphochloride	d	-	-	-	-
Silicon tetrachlor.	d	I	I	I	I
Stannic chloride	I	I	I	I	I
Water	I	I	I	s	I
Hot water	I	I	I	I	I

Table No.2.

<u>Solvents</u>	<u>Copper camphor- ate</u>	<u>Lead camphor- ate</u>	<u>Zinc camphor- ate</u>	<u>Mangan- ese cam- phorate</u>	<u>Nickel camphor- ate</u>
Acetic acid	s	s	s	s	s
Acrylic acid	s	s	s	s	s
Benzoic acid	s	s	s	s	s
Butyric acid	s	s	s	s	s
Propylic acid	s	s	ss	s	s
Stearic acid	s	s	s	s	s
Valeric acid	s	s	I	s	I
Valeric aq.	s	s	s	s	s
Monochlor ethyl acetate	I	I	I	s	I
Acetaldehyde	ss	I	I	I	I
Paraldehyde	ss	I	I	I	I
Benzoic anhydride	s	s	s	s	s
Acetamide	I	ss	I	ss	ss
Formamide	s	s	s	s	s
Amylamine	S	I	s	s	s
Ethylene diamine	d	ss	S	S	ss
Sodium acetate	I	I	I	ss	I
Potassium acetate	ss	ss	ss	ss	ss
Ammonium acetate	s	s	s	s	s
Ammonium hydroxide	s	s	s	s	s
Ammonium sulphate	s	s	s	s	s
Water	I	I	I	S	I

In general, the camphorates dealt with in this experiment are insoluble in the esters, hydrocarbons, ketones, aldehydes, alcohols, phenols, oils, nitriles and bases, and soluble in the acids. They are then characterized by a great insolubility. Excepting the acids, by far the greatest number of compounds which dissolve these camphorates contain an ammonium radical or an ammonia residue. The order of their solubilities is about the same, for if one salt is found to be soluble in a certain solvent the other four generally dissolve also, and to about the same extent. The following exceptions to the last statement, however, are to be noted. Manganese camphorate alone is soluble in cold water and in monochloracetate. In acetamide the copper and zinc salts are insoluble. The lead salt alone fails to dissolve in amylamine. Valeric acid does not dissolve zinc and nickel camphorates, yet upon the addition of a little water these are readily dissolved.

When a portion of copper camphorate, the size of a pin head, is added to ethylene diamine, the salt acquires a deep blue color and appears not to go into solution even on heating. If a larger quantity, say 0.1 gram, of the salt is added a vigorous reaction takes place with a sizzling sound. The solid becomes colored as before and a sufficient amount of it goes in solution to give the clear supernatant liquid a strong blue color. This new compound is soluble in water, imparting to the water in very dilute

solutions a violet color, in stronger solutions a deep blue color. Ethylene diamine is able to convert more than its volume of copper camphorate into the water soluble compound. It is apparently an addition product. No further work was done on this reaction. Whether any of the other camphorates behave similarly was not so easily determined, excepting that manganese camphorate is soluble, so that has been deferred until more time is available.

The great insolubility of these camphorates can be said to be due neither to the camphorate radical nor to the metallic radical, but rather to both; for some of the camphorates (e.g. those of sodium and potassium) are known to be soluble and, on the other hand, metallic soaps, such as lead and manganese oleates and stearates, and metallic resinates, such as lead and manganese resinates, are soluble in benzene. The solubility in the acids is probably due to a double decomposition, whereby the metallic radical is carried in in combination with the acid radical of the solvent and the camphorate radical as camphoric acid; e.g., copper camphorate probably reacts with acetic acid to form copper acetate and camphoric acid in solution. This is possible since both copper acetate and camphoric acid are soluble in acetic acid. That these camphorates are insoluble in camphoric acid itself leads to the same conclusion, for the camphorates, if soluble as such in the acids,

would be apt to be soluble in camphoric acid. A solution of copper camphorate in aqueous ammonia has the same deep blue color of the inorganic salts of copper in ammoniacal solution. Copper camphorate in amylamine also produces a deep blue solution, while in other solvents the color is much less pronounced. Apparently then a complex copper ammonia compound, or rather copper amine compound, is formed. If a new compound is formed it is soluble in an excess of the solvent in contrast with the behavior of ethylene diamine, in which the new compound was found to be only sparingly soluble in an excess of the solvent. The solution of copper camphorate in amylamine conducts no better than amylamine itself.

If the above assumption in regard to the solution of copper camphorate is correct, it is to be expected that zinc and nickel camphorates should dissolve in amylamine, since these two metals form complex ammonia salts. The fact that manganese forms double ammonium salts in aqueous solutions does not explain the solution of manganese camphorate in amylamine, since it is apparent that we do not have a parallel case. The claim of some chemists that they have obtained complex ammonia salts of manganese is supported by the fact that manganese camphorate dissolves in amylamine and ethylene diamine as noted above. Similarly to manganese, magnesium forms double ammonium salts, hence we might expect magnesium camphorate to be soluble in

amylamine if the solution of the manganese camphorate is not due to the formation of the complex salt. Surely this can not be predicted with any degree of certainty, for many of the above cases must be due to the specific properties of the salt and solvent and not to a general property of the salts or solutions. That the camphorates dissolved in fused ammonium salts is to be expected since these salts on fusion decompose into ammonia and an acid.

A solution of copper camphorate in benzoic anhydride, when heated nearly to its boiling point, changes its color from blue to yellowish brown.

Approved

L. D. Kellum
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